

**PROCESS FOR LONG CRYSTAL LATERAL GROWTH IN SILICON
FILMS BY UV AND IR PULSE SEQUENCING**

**Invented by
Apostolos T. Voutsas
Robert S. Sposili
Mark A. Crowder**

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BACKGROUND OF THE INVENTION

The present invention relates generally to methods of
5 forming polycrystalline thin films and, more particularly, to methods
using laser annealing and lateral crystallization.

Polycrystalline silicon thin films are used to form thin-film
transistors (TFTs) for pixel-switching elements and other integrated
circuits that are simultaneously fabricated on display substrates. These
10 thin films and TFTs can provide for the fabrication of integrated circuits
on various substrates, for example, glass, plastic, or metal. These thin
films and TFTs may also be used for non-display applications as well.
Possible non-display applications include, sensors, ASICs, memory
modules, or printer heads, for example.

15 Polycrystalline silicon, also known as poly-Si, films may be
produced by crystallizing amorphous silicon, or microcrystalline silicon.
Quality poly-Si films can be produced using lateral growth processes, also
referred to as lateral crystallization. Quality poly-Si films can then be
used to produce high performance poly-Si TFTs. The quality of the films
20 and the resulting TFTs depends to a great extent on the crystal
characteristics. Laser induced lateral crystallization, which uses an
excimer laser to crystallize amorphous silicon such that the crystal grows
in a lateral direction, has been used to produce quality poly-Si films. By
moving the laser and sequentially exposing adjacent regions it is possible

to form polycrystalline films having long crystal grains oriented in the scanning direction.

Despite the success of laser-induced lateral crystallization, and related crystallization techniques, in producing quality poly-Si materials problem areas persist. There is a continued lack of uniformity in the material characteristics of the films produced. The lack of uniformity results, in part, from the formation of sub-boundaries along the direction of lateral growth. The sub-boundaries generate trap states within the active layer, which may modulate device operation resulting in non-uniformity in device characteristics, including threshold voltage. Another problem is related to the lateral growth length (LGL), which is the distance that the crystal grows laterally for each laser shot. The LGL is currently limited to between approximately less than 3 – 5 μm . This LGL limitation also affects techniques that employ sequential crystallization by scanning, because the moving pitch (p) between sequential laser shots is even more restricted in that the moving pitch should be less than the LGL, ($p < \text{LGL}$). Crystallization over lengths of between about 30 μm and 100 μm , which is desired for device fabrication, requires many shots, which translates to longer process times and reduced productivity.

SUMMARY OF THE INVENTION

Accordingly, a process is provided to increase the LGL. The method may also simultaneously increase the spacing between sub-boundaries, thereby reducing the sensitivity of device characteristics to non-uniformity issues caused by sub-boundaries.

The process of lateral crystallization comprises providing a silicon film on a substrate surface. A localized substrate region at the substrate surface is exposed to a laser heating source. The laser heating source may be a CO₂ laser for example. A portion of the silicon film in thermal contact with the localized substrate region is crystallized by irradiation from a laser annealing source. The laser annealing source may be a UV laser, such as an excimer laser, or a visible laser, such as a frequency-doubled solid state laser.

BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 is a temperature history plot for a silicon film.
Fig. 2 is a temperature history plot for an SiO₂ substrate.
Fig. 3 illustrates a process sequence.
Fig. 4 illustrates a process sequence.
Fig. 5 illustrates a process sequence.
Fig. 6 illustrates a repeating process sequence.
Fig. 7 is a chart of lateral growth length versus substrate temperature.

DETAILED DESCRIPTION OF THE INVENTION

A theoretical study of the physics of laser annealing reveals that the lateral growth length (LGL) is related to the time that the molten Si film can remain at, or slightly above, a temperature range that prohibits nucleation from occurring within undercooled, molten silicon. The temperature range below which nucleation occurs may be referred to herein as the nucleation temperature. The temperature of the Si during crystallization depends, in part, on the rate of heat loss from the

irradiated domain. The irradiated domain refers to that portion of the silicon film that is irradiated during laser annealing. Slower heat loss will correspond to a longer time period at, or above, the nucleation temperature. The longer the time period that the Si within the irradiated domain is above the nucleation temperature, the longer the resulting lateral growth length will be.

Increasing the steady-state temperature of the substrate will reduce the rate of heat loss from the cooling molten-Si film. Fig. 1 illustrates a temperature history of laser-irradiated Si films corresponding to three substrate temperatures. Temperature history refers to a plot of temperature versus time at a specific location within the irradiated domain. Fig. 1 shows plots of the temperature history at the surface of an irradiated domain of Si film. The first temperature history 12 is for a silicon film over a substrate at room temperature, about 300 K. The second temperature history 14 is for a silicon film over a substrate at about 900 K. The third temperature history 16 is for a silicon film over a substrate at about 1200 K. Generally, the three plots show some common patterns for films irradiated by a laser pulse. The laser pulse heats the Si film rapidly increasing its temperature within several nanoseconds, melting the irradiated region of the Si film. The laser pulse may be between 30 and 300 nanoseconds long, and was 30 nanoseconds in the examples shown in Fig. 1. Once the laser pulse ends, the temperature of the molten Si film continues to climb, in response to the energy that has been pumped into the film by the laser pulse until a maximum temperature is reached. The temperature value at the maximum point depends on several factors, including the laser fluence, the substrate temperature, the pulse duration, and the film thickness, along with other

factors. Since heat is removed by conduction through the bottom of the irradiated domain, and the surrounding unmelted film, as well as radiation from the top surface, the temperature of the irradiated domain will reach its maximum value and then decline as heat is removed from the irradiated domain. Conduction tends to dominate the heat removal process. As the temperature in the molten Si region falls below the formal melting point of the film, lateral growth occurs in the film. The formal melting point refers to the established melting point of a bulk material, for example bulk silicon. The molten Si that exists at temperatures below its formal melting point is referred to as undercooled liquid. Such liquid can exist at temperatures substantially below the formal melting point. For example, crystalline silicon has a formal melting point of 1410 °C, yet undercooled Si can exist at temperatures as low as approximately 900 °C. Lateral growth continues as the temperature continues to decline.

However, the probability of nucleation is related to the amount of undercooling in the molten-Si. The lower the temperature of an undercooled liquid, the higher the probability of nucleation occurring within the liquid molten-Si. Nucleation disrupts the lateral growth process and thereby limits the lateral growth length. When nucleation occurs, release of latent heat momentarily increases the temperature in the recrystallized Si film, which manifests as a hump on the temperature history. Although the nucleation temperature is not fixed, since nucleation is a stochastic process of temperature and time, it is possible to identify a temperature band within which the probability for nucleation is high enough to interfere with lateral crystallization processes. This band has been empirically determined to be in the range of between approximately 1200 K and 1300 K. The horizontal dashed line in Fig. 1

corresponds approximately to the center of this band. After the molten Si film completely transforms to solid-Si, by pure lateral growth or a combination of lateral growth and nucleation processes, the temperature continues to drop as shown in Fig. 1.

5 Comparing the three temperature history plots at three different substrate temperatures shows the profound effect that the temperature of the substrate has on the characteristics of the temperature history of the film. Higher substrate temperatures prolong the average quench time, which is the time the molten-Si remains at temperatures
10 above the band corresponding to high nucleation probability. The average quench time 18 for the case of the substrate at approximately 1200 K is shown. The higher substrate temperature also decreases the solidification velocity, which is the velocity of the advancing solid interface. The solidification velocity is given by the slope of the temperature history
15 curve, which is shown at 22 for the case using an approximately 1200 K substrate temperature, and is related to the propensity of the material for defect formation. The higher substrate temperature also increases the sub-boundary spacing. Sub-boundary spacing on the order of 2 – 5 μm can be obtained as the substrate temperature approaches the Si melting point.
20 In contrast, the sub-boundary spacing is only on the order of 0.2 – 0.5 μm for substrate temperatures corresponding to room temperature. The longer the film is maintained below the formal melting point, but above the band corresponding to high nucleation probability, the longer the LGL achieved.

25 Although the benefits of using a high substrate temperature, for example greater than 1200 K, are clear, these temperatures are incompatible with glass substrates commonly used for display substrates.

It is impractical to maintain display glass at steady state temperatures that exceed approximately 600 °C.

However, if the period of heating is sufficiently short and the heated area sufficiently small, the high temperature will not cause significant damage to the substrate while still providing some of the benefits of higher substrate temperatures. For example, if the glass substrate immediately under the irradiated domain of the Si were heated for a sufficiently short period of time, the benefits of higher substrate temperature can be obtained, without causing significant substrate damage. Significant damage means substrate damage sufficient to prevent further processing, or render the substrate wholly unusable for its intended purpose. A certain amount of degradation of the substrate may therefore be acceptable, even if it may affect performance parameters or production yield.

In one embodiment of the present method, a first laser source is used to irradiate the silicon film, and a second laser source is used to heat the underlying substrate. Since Si absorbs strongly in the UV – visible range, for example below 0.8 μm , the first laser source will preferably emit in this UV – visible range. Excimer lasers are viable candidates for use as the first laser source. SiO_2 , and glass, such as borosilicate glass, for example CORNING 1737, absorb strongly in the far-IR region, from about 9 to 11 μm . The second laser source preferably emits in this far IR region. CO_2 lasers are commercially available at wavelengths of 10.6 μm , which make them suitable candidates for the second laser source.

The primary parameters that control the peak temperature and temperature history of a substrate for a single CO_2 laser pulse

include, the instantaneous power (energy/time), the instantaneous power density (instantaneous power/area), and the fluence (instantaneous power density times pulse duration, which corresponds to energy/area/pulse). In some laser systems the instantaneous power is a fixed parameter. In this case, the instantaneous power density (IPD) can be adjusted by adjusting the beam area. Similarly, the fluence can be adjusted by adjusting the beam area and by controlling the pulse duration. Decreasing the beam area increases both the IPD and the fluence. However, the fluence can be controlled independently from the IPD by adjusting the laser pulse duration.

If multiple laser pulses are being used to heat the substrate, the average power density may also affect the temperature history. The average power density corresponds to the fluence times the repetition rate, which also corresponds to the instantaneous power density times the duty cycle. The duty cycle is the fraction of time that the CO₂ laser is actually firing. The average power density can be controlled by adjusting the beam area, which affects both the fluence and the IPD, by adjusting the pulse width, which affects the fluence, or by adjusting the repetition rate, which affects the duty cycle and the average power density independent of the fluence or the IPD.

In sequential lateral solidification processes, the annealing laser source is moved by a scanning distance, which is some fraction of the lateral growth length (LGL) between annealing exposures. If the substrate is continuously scanned, the annealing laser source may be fired as the desired scanning distance is reached. In an embodiment of the present method, the CO₂ laser may be scanned along with the annealing exposure. This results in a given region of the substrate being exposed

multiple times as the scan progresses. Accordingly, the cumulative average power density will affect the temperature history of the substrate. The cumulative average power density is the average power density times the number of shots that a given point is exposed to. In an embodiment of the present method, wherein there is one CO₂ laser shot per annealing laser shot, the number of shots is defined by the distance across the beam in the scanning direction divided by the step size of the CO₂ laser.

In another embodiment, multiple CO₂ laser shots will be made between annealing laser shots as the substrate is continuously scanned. In this case, the number of shots is still determined by the distance across the beam in the scanning direction divided by the step size of the CO₂ laser. The CO₂ laser may not have the same step size or distance across the beam as the annealing laser.

In another embodiment, the substrate is scanned in discrete steps and multiple CO₂ laser shots will be made between annealing laser shots. In this case, the number of shots may be determined by multiplying the number of CO₂ laser shots between scanning steps times the distance across the CO₂ beam in the scanning direction divided by the CO₂ laser step size.

Fig. 2 shows the temperature history for three pulses, using a 1mm² beam area for these examples. The pulses are characterized by pulse duration and fluence. The first curve 32 corresponds to a 400 μs pulse at 15 mJ/mm². The second curve 34 corresponds to a 400 μs pulse at 10 mJ/mm². The third curve 36 corresponds to a 100 μs pulse at 4 mJ/mm². From these given values for each example pulse, it would be possible to calculate the IPD. For these examples the time between pulses was approximately 3 ms, so the average power density may also be

determined. The instantaneous power was not fixed for the purpose of these examples, which illustrate achievable temperatures and the affect of certain control parameters on the temperature histories. The temperature histories shown in Fig. 2 do not take into account substrate scanning.

By reviewing a temperature history, similar to those shown in Fig. 2, it will be possible to approximately select an effective substrate temperature at which the annealing process will occur. According to an embodiment of the present process, the Si film and any supporting layers, including an SiO₂ substrate, a glass substrate, or an SiO₂ layer overlying a glass substrate, in contact with the Si film, are irradiated by two localized irradiation sources. One source is a UV – visible source suitable for crystallizing the Si film. The other source is suitable for heating the SiO₂ substrate. The two sources have a temporal offset, which may be used to select the effective substrate temperature for the irradiated domain for a known peak temperature and temperature history.

In one embodiment, for example, a CO₂ laser is used as a laser heating source to heat the SiO₂ layer under the Si film. The Si film is irradiated using either a UV laser, such as an excimer laser or frequency-tripled solid-state laser, or a visible laser, such as a frequency-doubled solid-state laser, as a laser annealing source. A XeCl laser at 308 nm or a KrF laser at 243 nm are possible candidates for the excimer laser. Frequency-tripled solid-state lasers, such as tripled Nd-YAG lasers or tripled Nd-YVO₄ lasers, are also possible candidates for the UV laser. Frequency-doubled solid-state lasers, such as doubled Nd-YAG lasers operating at 532 nm or doubled Nd-YVO₄ lasers, are possible candidates for the visible laser.

Fig. 3 schematically illustrates one embodiment of the present process. Two idealized laser pulses are shown. The CO₂ laser pulse 42 starts and heats the SiO₂ substrate. Some time later the excimer laser pulse 44 irradiates the Si layer to crystallize it. The time between the start of the CO₂ laser pulse and the start of the excimer laser pulse, also known as the temporal offset (τ_{pre}), can be used to establish the effective substrate temperature at the time of the excimer laser pulse for a given temperature history. In this example, both the CO₂ laser pulse and the excimer laser pulse are irradiating the same area at the same time for a period of combined irradiation, τ_{comb} . During τ_{comb} , it is possible for the molten-Si film to absorb energy from both the excimer laser and the CO₂ laser. This is because although solid Si is practically transparent to IR radiation, molten-Si absorbs IR radiation. The total fluence of the two beams may need to be adjusted to avoid agglomeration of the Si film. The CO₂ laser pulse may remain on for a period, τ_{post} , after the excimer pulse has ended. Some absorption from the CO₂ laser pulse may continue to occur within the molten-Si film. This absorption, along with the elevated substrate temperature reduces the quenching rate in the Si film and increases the effective time period for lateral growth, thereby increasing the maximum possible lateral growth length.

Fig. 4 schematically illustrates another embodiment of the present process. Two idealized laser pulses are shown. The CO₂ laser pulse 42 starts and heats the SiO₂ substrate. Some time after the CO₂ laser pulse ends the excimer laser pulse 44 irradiates the Si layer to crystallize it. The time between the start of the CO₂ laser pulse and the start of the excimer laser pulse, also known as the temporal offset (τ_{pre}), can be used to establish the effective substrate temperature at the time of

the excimer laser pulse for a given temperature history of the substrate based on the CO₂ laser parameters. Since there is no overlap between the two laser pulses, the Si film will absorb radiation from the excimer laser pulse separately from the CO₂ laser. The Si film will be effectively
5 transparent to the CO₂ laser pulse and so will not absorb a significant amount of the CO₂ laser pulse. This scheme decouples the effect of the two different sources, while still providing an effective substrate temperature that will prolong the quenching time. Assuming that the fastest of the two lasers discharges at a frequency (f), the temporal offset
10 (τ_{pre}) between the two pulses will be loosely constrained by the following relations: $\tau_{CO_2} \leq \tau_{pre} < 1/f - \tau_{fast}$, where τ_{fast} is the duration of the fast discharge.

Figure 5 schematically illustrates another embodiment of the present process. Two idealized laser pulses are shown. The CO₂ laser
15 pulse 42 starts and heats the SiO₂ substrate. Some time before the CO₂ laser pulse ends the excimer laser pulse 44 irradiates the Si layer to crystallize it. The time between the start of the CO₂ laser pulse and the start of the excimer laser pulse, also known as the temporal offset (τ_{pre}), can be used to establish the effective substrate temperature at the time of
20 the excimer laser pulse by referring to the temperature history of the substrate related to the laser pulse. The excimer laser pulse 44 continues beyond the end of the CO₂ laser pulse. In this example, both the CO₂ laser pulse and the excimer laser pulse are irradiating the same area at the same time for a period of combined irradiation, τ_{comb} . During τ_{comb} , it
25 is possible for the molten-Si film to absorb energy from both the excimer laser and the CO₂ laser. This is because although solid Si is practically transparent to IR radiation, molten-Si absorbs IR radiation. The total

fluence of the two beams may need to be adjusted to avoid agglomeration of the Si film. The excimer laser pulse may remain on for a period, τ_{post} , after the CO₂ laser pulse has ended.

The excimer laser pulse will temporally correspond
5 approximately to the maximum effective substrate temperature if the excimer laser pulse is timed to coincide with the end of the CO₂ laser pulse as shown in Fig. 5, or after the end of the CO₂ laser pulse while the temperature of the substrate and film continues to increase after the end of the CO₂ laser pulse. In an embodiment of the present method, the
10 temporal offset is determined so that the excimer laser pulse corresponds to approximately the maximum effective substrate temperature, and the maximum effective substrate temperature is controlled by adjusting the energy introduced into the substrate, which determines the temperature history. As discussed above, the energy introduced into the substrate by
15 the CO₂ laser can be controlled by adjusting a number of factors. The instantaneous power could be adjusted in some embodiments. The beam area could be adjusted to increase or decrease the IPD and the fluence. The pulse duration could be used to vary the fluence separately from the IPD. The repetition rate, or the corresponding duty cycle, could be
20 adjusted to control the average power density for multiple laser pulses, independent from the factors related to each individual pulse. And in the case of scanning applications the cumulative average power density of multiple scanned shots may be further adjusted by varying the stepping distance relative to the beam dimension in the scanning direction.

25 Since the CO₂ laser pulse may be heating a localized region of the substrate to a temperature above its formal melting point, it is preferred to provide a spatial alignment of the laser annealing source and

the CO₂ laser pulse to maximize the overlap of the two sources. In this manner the maximum thermal energy of the CO₂ laser pulse may be used so as to provide the desired benefit without introducing additional unused heat to the substrate. The formal melting point refers to the steady state
5 melting point of bulk material, which as discussed herein may be exceeded in a localized area for a short period of time without causing significant damage to the substrate.

With any of these pulse sequences, the rate of temperature change in the substrate is sufficiently slow relative to the annealing
10 source that the substrate has a substantially constant substrate temperature over the approximately 30 ns – 300 ns pulse duration of the annealing source plus the subsequent approximately 200 ns – 500 ns for resolidification. This is apparent by reviewing the difference in the time scale between Fig. 1 and Fig. 2. Accordingly, it is possible to establish the
15 effective substrate temperature using a given laser pulse from the laser heating source, for example the CO₂ laser, by determining the temporal offset (τ_{pre}), corresponding to the desired substrate temperature based upon the temperature history of the substrate surface. Similarly, for a given temporal offset the CO₂ laser pulse sequence may be adjusted to
20 achieve the desired substrate temperature at the time of the annealing laser pulse.

A range of values may be suitable for practicing one or more embodiments of the present method. The CO₂ pulse area is preferably matched to the excimer beam area, although larger or smaller beams may
25 be used. CO₂ pulse instantaneous power may be selected so as to provide a desired instantaneous power density based on the beam area used. The following ranges of values may be used as general guidelines:

CO₂ pulse duration: 5 – 1000 μ s, preferably 5-100 μ sec, or
5 – 30 μ sec.

CO₂ pulse area: 1 mm² – 1 cm²

CO₂ pulse instantaneous power density: 50 – 150 W/mm²

5 CO₂ pulse fluence: 0.4 – 4 J/cm²; more preferably
0.4 – 1.5 J/cm²; even more preferably 0.4 – 1 J/cm².

Excimer pulse duration: 30 – 300 ns

Pulse frequency (f): 100 – 300 Hz.

Temporal offset (τ_{pre}): 5 – 1500 μ s

10 Fig. 6 shows a repeating pulse sequence corresponding to
that shown in Fig. 3 for purposes of a scanning crystallization process.
The sequences shown in Figs. 4 and 5 could be similarly repeated for use
in scanning crystallization processes.

Lateral growth in Si films using an example of the present
15 process has been found to be substantially longer than without the laser
heating source. For example, using a CO₂ laser with a pulse duration of
70 μ s and a fluence of 0.5 – 2 J/cm² and an excimer laser pulse with a
temporal offset of approximately 60 to 70 μ s, a lateral growth length of 20
to 25 μ m can be obtained. The same excimer laser pulse without the use
20 of the CO₂ laser, and a substrate at room temperature, produced a lateral
growth length of approximately 2 μ m. For 50 nm-thick Si films, a sub-
boundary spacing of 2 μ m has been observed, which is a factor of eight
improvement over that obtained without the use of a laser heating source.

Fig. 7 is a graph showing the computed dependence of lateral
25 growth length as a function of effective substrate temperature, using an
XeCl excimer laser at 308nm with a 500 mJ/cm² laser fluence as the laser
annealing source, and assuming a single isolated laser heating pulse.

Obtaining long lateral growth lengths is a matter of balancing the effective substrate temperature against the potential damage to the substrate as a result of extended exposure to extreme temperatures, even for short periods of time within localized regions.

5 Several embodiments of the present process have been described. Since modification of these processes will be apparent to those of ordinary skill in the art, the following claims shall not be limited to any specific embodiment.

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